

12 **EUROPEAN PATENT APPLICATION**

21 Application number: **90301208.6**

51 Int. Cl.⁵: **C11D 17/00, C11D 3/37**

22 Date of filing: **06.02.90**

30 Priority: **09.02.89 GB 8902909**

43 Date of publication of application:
16.08.90 Bulletin 90/33

64 Designated Contracting States:
CH DE ES FR GB IT LI NL SE

71 Applicant: **UNILEVER PLC**
Unilever House Blackfriars
London EC4P 4BQ(GB)
84 **GB**

Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)
84 **CH DE ES FR IT LI NL SE**

72 Inventor: **Akay, Galip**
36 Gulls Way
Heswall, Wirral L60 9JQ(GB)

74 Representative: **Ford, Michael Frederick et al**
MEWBURN ELLIS 2 Cursitor Street
London EC4P 4BQ(GB)

54 **Coating Process.**

57 A coating process can serve to encapsulate either solid particles or liquid droplets or both. The process comprises a first step of forming a melt of a coating material in which the solid particles or liquid droplets as a dispersed phase. This melt is then destabilised by adding solid particles and/or by cooling. This causes the melt to crumble to a particulate product consisting of dispersed phase encapsulated with the coating material.

Examples of coating material are organic polymers, soap fatty acid mixtures and non-soap surfactants. Materials which can be encapsulated include bleaching agents and perfume.

COATING PROCESS

This invention relates to a novel agglomeration, coating or encapsulation process. The process has a wide range of applications. It can be applied to coating or encapsulating solid particles, liquid droplets or a mixture of the two.

In a first aspect the invention provides a process for coating or encapsulating solid particles and/or liquid droplets, the process comprising a first step of forming a melt of a coating material with the said particles and/or droplets as a disperse phase therein, and a second step of destabilizing the melt by addition of solid particles and/or by cooling, causing the melt to crumble to a particulate product whereof the particles comprise the coating material with the particles and/or droplets of the disperse phase embedded therein. The coating process may serve as a means of agglomeration of disperse phase particles.

A second aspect of this invention is the particulate products of the process.

Our European application EP-A-303416 which is not a prior publication discloses a form of the present invention carried out using polyalkylene or copolymers with at least 70% polyalkylene therein as the coating material, while using water-insoluble inorganic abrasive material to provide both the particles which are coated and particles which destabilize the melt.

Certain forms of the present invention therefore do not include the combination of water-insoluble solid particles as the sole disperse phase and polyalkylene or alkylene copolymers with not more than 30% of other monomers containing a carboxylic acid or ester group as the organic polymeric material.

Essential to this invention is the finding that a melt containing a sufficient quantity of a disperse phase can be induced to crumble to a particulate state in which the disperse phase is embedded in particles of what was previously the continuous phase. Crumbling occurs when the amount of disperse phase present exceeds the amount which the continuous phase is able to support. It can be induced by cooling - which reduces the ability of the continuous phase to support disperse phase - or by direct addition of some material which adds to the total amount of disperse material. Combination of cooling and addition of solid disperse phase is most effective since the solid material causes crumbling locally and cooling fortifies this phase separation.

The coating material which forms a melt will generally be one or more organic compounds. It may especially be provided by an organic polymeric material which melts at a temperature above ambient. Another possibility is that the coating material is waxy, e.g. paraffin wax. A further possibility is that the coating material is an organic compound which contains alkyl groups of detergent chain length, i.e. 8 to 20 carbon atoms, as in a surfactant, soap or fatty acid.

An advantage of the present invention is that it is effective for coating or encapsulating small particles, and mixtures of particles displaying a range of particle sizes. Some known coating processes, such as fluidized beds, are least effective with small particles.

The invention can be used to coat or encapsulate a range of materials and by doing so can serve a variety of useful purposes depending on the nature of the encapsulated material and the polymeric coating material.

A characteristic of the invention is that solvent is often not employed, so that the product does not contain traces of solvent.

Since the invention can be implemented in a wide variety of ways, it is convenient to describe a straightforward example in general terms, by way of illustration, before proceeding with more general discussion. This example consists in coating sodium chloride with polyethylene glycol having an average molecular weight of 20,000. The final product contains, by weight:

polyethylene glycol (PEG 20,000)	25%
sodium chloride	65%
silica, mean particle size $7 \times 10^{-9} \text{m}$	10%

Initially the polyethylene glycol is heated to somewhat above its melting point. The sodium chloride, as fine crystals, is mixed into the molten polymer forming a disperse phase in the melt. The melt is now cooled to slightly above the melting point of the polymer. The silica is mixed in and the mixture allowed to cool further. The melt crumbles into particles. These particles are mostly agglomerates of sodium chloride

crystals embedded in solidified polymer, with silica mainly at the exterior of these particles.

The materials in the above example are thus an organic polymeric coating material which in the above example was polyethylene glycol, a solid disperse phase which was sodium chloride and a "crumbling agent" which was silica. The term "crumbling agent" is used because it causes the melt to crumble into particulate form.

In order that a coating material should form an effective coating of another material, it should be adequately compatible with it. Where this is lacking, phase separation or weak, easily removed coatings result. When appropriate, compatibility can be enhanced by any of:

- (i) coating a solid disperse phase with silane or titanate coupling agents (which are known per se)
- (ii) inducing bonding between the coating material and the disperse phase
- (iii) including surfactant to form a "bridge" at the interface between disperse phase and coating material.

Some surfactants may also be incorporated into the coating material, or used as coating material. When more than one coating is to be employed, surfactant can form a "bridge" to enhance the compatibility of the coating materials.

In the process of this invention it is not essential that the disperse phase be solid. As an alternative, or in addition, a liquid disperse phase may be employed. This may be liquid at ambient temperature, or it may be a material which is solid at ambient temperature but is sufficiently low melting that it is liquid at the temperatures of processing.

Further possibilities are that liquid may be incorporated into the pores of a porous disperse phase, or liquid may be dispersed in coating material applied to a solid disperse phase. Indeed it would be possible for liquid to be present in both the coating material and a porous solid disperse phase.

The process may be put to a number of uses. Possible applications include:-

Agglomeration of small particles into larger, more convenient, sizes. This could serve for instance to ameliorate dustiness or poor flow characteristics of finely divided material.

Protective coating of a material, protecting it from an adverse environment until the time of use. This could for instance serve to protect a chemically reactive material until it is used.

Delayed release of a material, or controlled slow release, due to the presence of a coating.

Conversion of a liquid into the form of a particulate solid. This for instance would enable incorporation of a liquid ingredient into a particulate solid product.

Grouping multiple materials together. This for instance could be used to prevent segregation of materials included in a particulate end product.

There are various developments of the basic process which may be employed:-

A preliminary coating of a liquid may be applied to a solid disperse phase. In particular such a preliminary coating may be coating of surfactant or of a liquid which includes a surfactant. Such a preliminary coating may serve to provide a desired degree of compatibility with the polymeric coating material. Another use for a preliminary coating on the solid disperse phase is to provide a barrier layer to isolate a potentially reactive solid disperse phase during mixing with polymer at elevated temperatures.

When a solid disperse phase is porous, a preliminary coating of a high molecular weight polymer may be used before coating with a lower molecular weight coating material in order that the porous solid does not absorb excessive quantities of the coating material.

Another development of the process is to apply multiple coating layers. In particular, particles may be encapsulated with a first coating material by a procedure in accordance with the invention after which a second outer coating may be applied either by use of a further procedure in accordance with the invention or by means of some other coating technique such as fluidized bed coating.

When two coatings are provided, one useful possibility is that the inner coating provides mechanical strength while the outer coating provides a barrier to protect the coated material from the surrounding environment. Another possibility is for the outer coating to be a water-insoluble coating (or a poorly soluble outer coating) applied over particles which are water-soluble or water-swellaable. Such an arrangement can serve to delay release of the encapsulated material when the particles are placed in water until such time as the water has penetrated the outer coating. Swelling of the inner particles when water does penetrate to them may at that point serve to rupture the outer coating so that after a delay caused by the outer coating the subsequent release is not restrained by the outer coating.

Within this general concept, one possibility is for the inner particles (that is to say the particles to which the second, outer coating is applied) to contain a water-swellaable crumbling agent. Another possibility is for these particles to contain as first coating material an organic polymeric material which is water-soluble or water-swellaable. In this latter case, the second, outer coating can serve to delay release of any part of the encapsulated dispersed phase until the outer coating is penetrated, after which dissolution or swelling of the

organic polymeric material within the particles controls the rate of release of the disperse phase.

Possibilities for materials will now be discussed.

5 Coating Material

One possibility for this is an organic polymer or copolymer which is suitable for the end use of the encapsulated disperse phase. The polymeric material needs to melt at a temperature which is suitable for incorporating the disperse phase. The material may be a mixture of polymers.

10 If it is desired to use a polymer of high melting point or which degrades before reaching its melting point, then a polymer of low molecular weight may be used as a solvent for the polymer. Alternatively some organic solvent may be used to form a viscous concentrated solution of the polymer.

Use of high molecular weight polymer may be advantageous in that less crumbling agent tends to be required.

15 Another possibility for the coating material is non-soap surfactant. This may, or may not, be surfactant derived from a polymer such as fatty acyl and fatty diacyl derivatives of polyethyleneglycol.

Another useful possibility for the coating material is a mixture of soap and fatty acid. Yet another possibility is waxy material such as paraffin wax with melting point above ambient temperature.

Blends of materials may be used in order to obtain desired properties of the coating material. These 20 blends may in particular be blends of two or more polymers, or blends of polymer(s) with non soap surfactants or with soap and fatty acid. For instance, surfactant may serve as solvent for high molecular weight polymer.

When the coating material is a blend of compatible materials, the melting and crystallisation behaviour of the components of the blend is modified. These properties of a blend can be determined by differential 25 scanning calorimetry.

Blends of materials may be chosen for release of the enclosed material to be brought about by any of: physical corrosion of coating,

solution of coating on exposure to water,

swelling of coating on exposure to water,

30 permeation of water through insoluble porous coating, possibly followed by rupture on swelling of encapsulated material,

exposure to specified temperature,

exposure to specified pH.

Examples of coating materials which may be used alone or in blends are:

35 1. Polyethylene glycol (PEG) and polyethylene oxide (PEO): This system provides a very extensive range of molecular weight ranging from a few hundreds to several millions. PEGs can be used by themselves as coating agent or may be used to dissolve other polymers.

2. Polyvinyl pyrrolidone (PVP): Generally used in combination with other polymers.

40 3. Poly (acrylic acid) (PAA):

Weak acid.

45 4. Cellulose acetate phthalate

(CAP): Weak acid.

5. Polyvinyl acetate phthalate

50 (PVAP): Weak acid.

Of use in

systems where

release of the

coated material

is dependent on

pH

6. poly (caprolactone) (PCL); poly (caprolactone) diol, (PCL-diol).

PCL has high permeability despite the fact it is not water soluble. May also be used to form blends with 55 other water soluble polymers.

7. Poly (ethylene-vinyl acetate) copolymer (EVAC-CP).

8. Poly (ethylene-acrylic acid) copolymer (EAA-CP).

9. Oxidised polyethylene (OPE): This polymer is used to provide compatibility between polyalkylenes

and water-soluble polymers or to modify the release characteristics of the other water-soluble polymers such as PEG's and PEO's.

10. Polyethylene glycol - fatty acid esters: These polymeric surfactants offer a wide range of melting point and water solubility/dispersibility depending on the length of the polyethylene glycol chain and fatty acid chain. For example the monolaurate of polyethylene glycol with average molecular weight 6000 has melting point of 61 °C and is highly water-soluble while the dilaurate of polyethylene glycol with average molecular weight 400 has melting point of 18 °C and is not water-soluble, merely water-dispersible. These materials can be used to provide two coatings which are compatible with each other but have different properties. PEG 6000 monolaurate can be used to provide a mechanically strong water-soluble first coating while PEG 400 dilaurate can be applied as a second coating forming a vapour barrier.

Blends of materials which have been found useful are:

1. Soap/fatty acid/polymer, especially sodium stearate/lauric acid/ethylene acrylic acid copolymer with a weight ratio 0.5 to 2.0 : 0.5 to 2.0: 1.

2. Fatty alcohol ethoxylate/polymer especially when the polymer is in lesser amount than the fatty alcohol ethoxylate and is polycaprolactone or ethylene acrylic acid copolymer.

In the first of these blends we have found that the presence of the polymer leads to a lowering of melting point, crystallinity and crystal size. It also modifies the water solubility. In the second we have found that inclusion of this or other polymers leads to an increase in melting point and in the hardness of the coating material.

Solid Disperse Phase

A wide variety of materials may be employed. Examples are sodium chloride, sodium carbonate, organic peroxy acids and their salts (bleaching agents), tetra-acetyl ethylene diamine (TAED, a low temperature bleach precursor), sodium perborate (bleaching agent), sodium dichloro isocyanurate dihydrate (SDCCA, a bleaching agent) and distearyl dimethyl ammonium chloride (a cationic surface active agent solid under the Trade Mark AROSURF TA-100).

Solid disperse phase particles may be porous, organic or inorganic, and may contain a liquid entrapped in the inter- or intra-particle pores. Examples of solid disperse phase particles are anhydrous sodium carbonate and porous silica. Liquids which may be carried by a porous disperse phase include antifoam agents and perfumes.

Liquid Disperse Phase

Again a wide variety of materials can be dispersed. Particular examples are silicone fluid (serves as a fabric softener) and a viscous dispersion of hydrophobed silica in silicone oil which serve as antifoam agent.

Crumbling Agent

The function of the crumbling agent is to enhance, locally or globally, the total amount of dispersed material beyond the point at which the molten system becomes unstable. The crumbling agent has to be solid at the temperature at which crumbling occurs and should not dissolve in the coating material at the temperature of processing. Subject to these constraints, a wide range of materials can be employed. Crumbling agents may be inorganic particulate solids, or may be particles of high molecular weight polymer. Other organic or inorganic particulate solids are not ruled out, but will generally be less economical and therefore are not preferred unless they have a specific function in the final product as discussed later. Crosslinked polymer powders and polymer latex particles may also be considered as crumbling agent. The effectiveness of a crumbling agent will be enhanced if its particle size is small. Examples of crumbling agents are:

Silica, anionic or cationic clays, zeolite, talc, sodium carbonate, sodium bicarbonate, calcite, polyethylene oxide (PEO), sodium carboxymethyl cellulose, starch, cellulose acetate, microcrystalline cellulose.

The crumbling agent may be provided by a further quantity of the material used as solid disperse phase (if any).

Much of the crumbling agent adheres to the surface of the particles formed by crumbling and it can therefore be used to modify the surface characteristics of these particles. For instance the crumbling agent

may confer hydrophilic or hydrophobic character and/or reduce the permeability of the coating to gases and vapours.

Crumbling agent in particles with a double coating can provide some important functions. In double coated particles most of the crumbling agent can be placed at the exterior of the particles with a single coating, which are formed before the application of the second coating. A different crumbling agent (inert) can be used to induce crumbling in the second coating step, if this step is carried out in accordance with the invention (rather than by using conventional coating techniques such as fluidized bed coating).

Other possible functions of the crumbling agent in double coat particles are summarised below:

1. Crumbling agent can absorb water, permeating through the outer coat, thus acting as a water sink to stop water affecting the encapsulated material during storage, or even provide delay in the release of the solid dispersed phase. Crumbling agents which can act as water sink are water soluble or water swellable polymers such as sodium carboxymethyl cellulose, clays, silica gels and inorganic salts which re-crystallise with large amounts of crystal water. Examples of such salts are sodium tripolyphosphate, sodium pyrophosphate, sodium orthophosphate, sodium polyphosphate glasses, aluminium sulphate $\text{Al}_2(\text{SO}_4)_3$ and sodium carbonate.

2. In addition to the anhydrous salts referred to above, inorganic salts such as LiI , LiBr , LiCl and AlCl_3 generate large amounts of heat upon hydration. Heat generated as a result of water absorption through the outer coat and hydration of the crumbling agent may serve to heal the surface cracks thus improving the storage stability of the capsules.

3. When water-swellable materials such as modified starches, cellulose, certain cross linked polymers or clays are used as crumbling agents they can also act as trigger agents to break the outer coat due to swelling of the crumbling agent upon contact with water permeating through voids in the outer coat.

4. Crumbling agent can also be a chemical which is to be delivered sequentially before the main dispersed solid phase which is encapsulated by the first coat.

Surfactants

As already mentioned, surfactants may be used as or included in the coating material. As well as this use of surfactants, surfactants may be included in order to emulsify a liquid disperse phase, or to effect surface modification of a solid dispersed phase. In emulsions involving silicone fluid or silicone antifoam, silicone glycol copolymer surfactants DC190, DC193 and DC198 (in particular DC193) supplied by Dow Corning were found to be a suitable surfactant. The surfactants DC193 and DC198 were also then used in the polymer phase which was the coating material. Presence of a surfactant to effect surface modification of a solid phase may in particular be utilised if the solid is not compatible with the coating material.

Outer Coating

If an outer coating is employed, i.e. a second coating onto previously coated particles, it may be composed of any coating material which is immobile at ambient temperature (or whatever temperature the final particles are to be kept at). Paraffin wax and poly(caprolactone)diol or poly(caprolactone)triol or their mixture are examples of materials which may be employed as an outer coating. Water soluble polymers such as polyethylene glycol may also be used.

Processing Procedure

The central step of the processing is the crumbling to particles. A melt of the organic polymeric material, containing disperse phase, is induced to crumble by cooling, addition of crumbling agent or some combination of both, while mixing is continued.

If a liquid disperse phase is used, this is preferably first emulsified in the coating material in a suitable mixing apparatus able to form an emulsion. The temperature must remain above the melting point of the coating material and if desired the liquid disperse phase may be preheated to above this temperature before adding to the mixer. The liquid disperse phase may be mixed with surfactant before being mixed with the coating material.

In one preferred procedure the coating material and additional surfactant (if required) are supplied to a suitable mixer and brought to a temperature above the melting point of the coating material.

If solid disperse phase is used, this is next added to the mixer and mixed into the molten polymeric material to form a homogeneous melt. This again is carried out at a temperature above the melting point of the polymeric material and if desired the solid disperse phase is preheated before it is added to the mixer. (Since a homogeneous melt is formed, a reversed order of addition to the mixer will generally be possible, if desired).

The temperature of the mix is now reduced to just above the melting point of the coating agent: 5 °C above the melting point is suitable. The crumbling agent is next added and the mixture is cooled further. It has been found convenient to add around 65% of the crumbling agent while holding the temperature just above the melting point of the polymeric material and then start cooling while adding the balance of the crumbling agent. Crumbling of the melt will generally commence before all of the crumbling agent has been added but the further addition of crumbling agent will complete the process and may bring about some further crumbling to smaller sized particles. It is desirable to continue mixing until the temperature has cooled to 30 °C less than the melting point of the coating agent. The particulate material which is produced may be subjected to a size reduction process at this stage if smaller particles are desired.

If the disperse phase is porous solid with liquid absorbed therein, it may be desirable to avoid the generation of severe stresses during mixing, because high stress could cause break up of the porous solid and release of the absorbed liquid. Low rotational speed mixing is then preferable.

It may be desirable to dose the molten coating material onto the solid disperse phase until melt formation commences and then start cooling and adding crumbling agent without waiting for the melt to become homogeneous.

The process of the invention can be carried out as a batch process, for instance using a Z-blade mixer, or as a continuous process, for instance using a twin screw extruder with more than one zone for introduction of material into the extruder. In a batch process, crumbling could be brought about in different apparatus to that used for initial melt formation.

Examples of the invention are set out below. Percentages and amounts are by weight unless otherwise stated.

These Examples are grouped as follows:

1.1 to 1.23 exemplify the basic process,
2.1 and 2.2 have a preliminary coating applied to the solid disperse phase,
3.1 is a double coating process in which the solid disperse phase melts during processing,
4.1 to 4.4 exemplify double coating processes in which the solid disperse phase does not melt. In Examples 3.1 and 4.1 to 4.4 the outer coating is water-insoluble and has a lower melting point than the first coating.

5.1 to 5.5 exemplify use of both liquid and solid disperse phases.

6.1 to 6.6 exemplify further coating materials.

Some discussion of particle sizes and properties is also given.

A number of materials are referred to by trade names or abbreviations. A key to these is as follows:

Coating Materials

PEG: Polyethylene glycol - number following PEG indicates molecular weight (Mw), ex Fluka AG
40 PEO: Polyethylene oxide - number following PEO indicates Mw, ex Aldrich
PVP: Polyvinylpyrrolidone - number following PVP indicates Mw, ex Aldrich
PCL: Poly(caprolactone); Melting point = 60 °C; ex Aldrich
AC680: Oxidised polyethylene, (Mw = 2000); ex Allied-Signal
AC400: Ethylene - vinyl acetate copolymer Mw = 3500, Vinyl acetate content = 30%; ex Allied-Signal
45 AC5120: Ethylene - acrylic acid copolymer, Mw = 3500, Acid number = 120mg KOH/g; ex Allied-Signal
Rigidex XGR 791: High density polyethylene homopolymer Mw = 1.1×10^5 ; ex BP Chemicals
PCL-diol: Poly(caprolactone)diol: Melting point = 45 °C, ex Aldrich
PAA 2000: Poly(acrylic acid). Number proceeding PAA indicates Mw; ex Aldrich
Paraffin Wax (49 °C): Wax with melting point of 49 °C, ex Fisons
50 PEG 6000 ML: Polyethylene glycol (molecular weight = 6000) monolaurate. Melting point = 61 °C; hydrophile - lipophile balance 19.2 (water-soluble); ex Stephan Europe
PEG 6000 DS: Polyethylene glycol (molecular weight = 6000) distearate. Melting point = 55 °C; hydrophile - lipophile balance = 18.4 (water-soluble); ex Courtaulds Chemicals
PEG 200 DS: Polyethylene glycol (molecular weight = 200) distearate. Melting point = 34 °C; hydrophile
55 - lipophile balance = 5.0 (dispersible hot in water); ex Courtaulds Chemicals
Synperonic A7: Ethoxylated alcohol. Pour point = 21 °C; hydrophile - lipophile balance = 12.2 (water dispersible) ex Shell Chemicals

Solid Dispersed Phase

TAED: Tetra-acetyl ethylene diamine, ex BDH

SDCCA: Sodium dichloro isocyanurate dihydrate, ex BDH

Arosurf TA-100: Distearyl dimethyl ammonium chloride (cationic surfactant with melting point approx 75 °C) ex Sherex

5 Light Soda Ash: Anhydrous and porous sodium carbonate (ex ICI) Particle size: 120µm; total intrusion volume: 1.14cm³/gram

Microsil GP: Porous silica (ex Crosfield Chemical) Particle size: 10µm; BET surface area: 210m²/gram

Crumbling Agents

Aerosil 380: Pyrogenic silica (ex Degussa), particle size 7nm

10 Aerosil R972: Pyrogenic hydrophobed silica (ex Degussa), particle size 16nm

Avicel PH-101: Microcrystalline cellulose (ex FMC Corp) particle size = 50µm

Starch: Particle size = 5µm, (ex BDH)

Bentone SD-2L: Clay, particle size <1µm (ex NL Chemicals)

TSPP: Tetrasodium pyrophosphate, ex BDH

Surfactants

Arquad 2HT: Di(hydrogenated tallowalkyl) dimethyl ammonium chloride, ex Akzo

DC 193: Silicone glycol copolymer, ex Dow Corning

Span 85: Sorbitone trioleate (a nonionic surfactant) ex ICI

20

Examples 1.1 to 1.23

A process was carried out using a variety of materials for the solid disperse phase and a variety of organic coating materials. In most of these examples surfactant was unnecessary and was not used. The procedure was the same in each case, except in Examples 1.22 and 1.23. The coating material was melted in a Z-blade mixer of 1Kg capacity equipped with heating and cooling facilities. The solid disperse phase was added at a temperature about 10 to 15 °C above the melting point of the coating material and after a homogeneous mix had been obtained, cooling of the mixture was started. When the temperature was within 5 °C of the melting point of the coating material 65% of the crumbling agent was added and then the temperature was held constant while mixing was continued to allow full incorporation of the crumbling agent. At this stage the mixture formed large agglomerates, and the remainder of the crumbling agent was added.

Motor torque, which was representative of viscosity, was monitored. It was observed that the torque rose steadily as the melt cooled towards the melting point of the coating material. When the crumbling agent was added the mixer torque dropped dramatically.

Mixing was continued while the temperature of the mixer was allowed to decrease to 30 °C below the melting point of the coating material over a period of 30 minutes.

Examples 1.22 and 1.23 used porous solid disperse phases with liquids absorbed by them. For Example 1.22 the disperse phase was light soda ash carrying absorbed silicone antifoam. For Example 1.23 the disperse phase was silica carrying absorbed perfume.

In these two examples the processing procedure commenced with solid disperse phase placed in the Z-blade mixer at a temperature about 10 °C above the melting point of the coating material. The coating material was added progressively at a temperature 5 °C above its melting point. As soon as a melt began to form, as indicated by formation of large agglomerates of the disperse phase, the crumbling agent was added and cooling of the mixer commenced. Again mixing was continued until the temperature had fallen to 30 °C below the melting point of the coating material.

In each of these examples the final product obtained had the appearance of a dry particulate solid.

The materials used in Examples 1.1 to 1.23 are set out in Table 1 below, which gives the amounts of the materials as percentages by weight of the final particulate composition.

50

55

TABLE 1

Example No	Coating Material(s)	Solid Dispersed Phase	Crumbling Agent
1.1	2% PEG 600 18% PEG 35000	60% TAED	20% TAED
1.2	2% PEG 600 18% PEG 4000	60% TAED	20% TAED
1.3	20% PEG 35000 5% PEO 200 000	60% TAED	15% AEROSIL 380
1.4	15% PEG 35000 5% PEO 200 000	75% TAED	5% AEROSIL 380
1.5	12% PEG 400 18% PVP 44000	60% TAED	10% AEROSIL 380
1.6	20% PCL 10% AC 680	65% TAED	5% AEROSIL 380
1.7	16% PEG 20000 8% PCL	60% NaCl	16% Starch
1.8	16% PEG 20000 8% PCL	60% NaCl	16% AVICEL PH-101
1.9	25% PEG 20000	65% TAED	10% AEROSIL 380
1.10	25% PEG 20000	65% TAED	10% BENTONE SD-2
1.11	20% PEG 20000 5% AC 400	65% TAED	10% AEROSIL 380
1.12	15% PEG 20000 10% AC 400	65% TAED	10% AEROSIL 380
1.13	15% PEG 20000 10% AC 5120	65% TAED	10% AEROSIL 380

TABLE 1 CONTINUED

Example No	Coating Material(s)	Solid Dispersed Phase	Crumbling Agent
1.14	20% PEG 6000 5% PAA 2000	65% NaCl	10% AEROSIL 380
1.15	10% PEG 6000 15% PAA 2000	65% NaCl	10% AEROSIL 380
1.16	25% PEG 20000	65% NaCl	10% AEROSIL 380
1.17	25% PCL	65% NaCl	10% AEROSIL 380
1.18	15% PEG 20000 10% PCL	65% NaCl	10% AEROSIL 380
1.19	25% PCL	60% SDCCA	10% AEROSIL R 972 5% AEROSIL 380
1.20	25% RIGIDEX XGR 791	65% SDCCA	10% AEROSIL 380
1.21	25% PCL-diol	65% Sodium Perborate	10% AEROSIL 380
1.22	7.5% Synper- -onic A7 4.5% PVP 40000 3.0% PCL diol	55% light soda ash 25% silicone antifoam	5% AEROSIL R972
1.23	20% PCL-diol	35% Microsil GP 40% perfume	5% AEROSIL 380

The porous disperse phase used in Example 1.23 was prepared by a route in which the porous silica (Microsil GP) was initially coated with a methoxyl functional silane coupling agent which forms a monolayer with a hydrophobic surface. The coupling agent was gamma-methacryloxypropyl trimethoxy-silane (A174, ex Union Carbide) with a monolayer surface coverage capacity of 314m²/gram. Since Microsil GP has a large surface area, full surface coverage requires large amounts of silane and it reduces the pore volume of silica. Therefore, only the surface and the outermost pores of Microsil GP were coated, following the procedure below:

The full water holding capacity of Microsil GP was determined to be 2.2 grams of water per gram of

silica. (Further addition of water resulted in the loss of free-flow of the powder). Silica particles were filled with water to 80% of their capacity. A sufficient amount of A174 silane coupling agent was dissolved in n-pentane to make up a solution able to occupy the rest of the pores left by water (i.e. 20% of the full absorbing capacity of the silica). When the n-pentane solution was added to the silica already wetted with water, the powder stopped being free-flowing. Subsequently the n-pentane was evaporated at room temperature and silane A174 polymerised at 38 °C and 70% relative humidity. The resulting surface-hydrophobed powder was then dried under vacuum at 60 °C for 24 hours before being allowed to absorb the perfume.

Examples 2.1 and 2.2

In these Examples, the surface of the solid dispersed phase was given a preliminary coating. The general procedure was that the solid dispersed phase was first mixed with a suitable preliminary coating material (i.e. surfactant or a liquid which may contain a surfactant) in a Z-blade mixer at an elevated temperature T_s . After a sufficient period of mixing at temperature T_s , the temperature of the mixer was reduced to some 10 °C above the melting point of the main (polymeric) coating material and this molten polymer was added to obtain a homogeneous mix. The temperature of the mixture was then reduced to a temperature t_c which is approximately 5 °C above the melting point of the polymer and 65% of the crumbling agent was added. Mixing was continued to allow full incorporation of the crumbling agent. At this stage, the mixture started forming large agglomerates. The remainder of the crumbling agent was added and the temperature of the mixer was allowed to drop 30 °C below the melting point of the polymer. The compositions of the coated particles prepared according to the above procedure are given in Table 2.

In the Example 2.1, only a surfactant was used to provide compatibility between NaCl and polymeric coating. In the Example 2.2, the solid dispersed phase was coated with a liquid mixture comprising a silicone fluid and a surfactant compatible with the solid dispersed phase and polymeric coating material. The function of the silicone fluid is to provide full surface coverage of the disperse phase and also to isolate the potentially reactive solid disperse phase during mixing with polymer at elevated temperatures.

TABLE 2

Example No	Polymeric Coating Material(s)	Surfactant System for Surface Coating of Solids	Solid Dispersed Phase	Solids Surface Coating Temp T_s (°C)	Crumbling Agent	T_c (°C)
2.1	7.5% PAA 2000	2% Arquad 2HT	65%	85	8%	65
	17.5% AC 5120		NaCl		Aerosil 380	
2.2	20% PCL	3% DC193	60%	80	5%	65
		12% Silicone Fluid (12500 cS)	SDDCA		Aerosil 380	

Example 3.1

Particles were prepared having compositions in accordance with Table 3 which also includes the relevant temperatures attained in the Z-blade mixer during various stages of the process. The process consisted of two stages. In the first coating stage solid dispersed phase and a polymeric coating material were melted together and mixed at a temperature T_{MAX-1} which was approximately 10 °C above the melting point of the solid dispersed phase. When a homogeneous melt was obtained, the melt was cooled down to the temperature T_{C1} which was just above the melting point of the first coating material. Some crumbling agent was added to induce crumbling. Cooling and mixing was continued until temperature was reduced to T_{MIN} which was below the melting point of the second coating material. The particulate product is now ready for the second stage of the coating process.

In the second stage of the coating process, the temperature was raised to T_{MAX-2} which was about 5-10 °C above the melting point of the second coating material which was added molten at the same temperature T_{MAX-2} while continuing to mix. In general when the agglomeration of particles is observed, it would be appropriate to reduce the temperature, and/or add some more crumbling agent. In this Example
5 more crumbling agent was added at the same temperature, after which the temperature was allowed to fall to some 30 °C below the melting point of the second coating material at a rate of approximately 1 °C per minute. The resulting particles consisted of solid dispersed phase particles encapsulated with a polymer coat over which another material formed an outer coat.

10

15

20

25

30

35

40

45

50

55

TABLE 3

Example No.	First Coating Stage (Solidification from Melt)						Second Coating Stage		
	First Coating Material(s)	Solid Dispersed Phase	Crumbling Agent	T _{MAX-1} (°C)	T _{Cl} (°C)	T _{MIN} (°C)	Second Coating Material(s)	Crumbling Agent	T _{MAX-2} (°C)
3.1	18% PEG 4000	58% Arosurf TA-100 (75°C)	8% Aerosil 380	85	60	40	10% Paraffin Wax (49°C) 2% Span 85	4% Aerosil 380	55

Examples 4.1 to 4.4

5

Particles were prepared having compositions in accordance with Table 4. These particles have two coatings in which the outer coat is water-insoluble and has lower melting point than the material in the first coat. In this respect these examples are similar to the Example 3.1 except that in the Example 3.1, the solid dispersed phase is melted with the first coat.

10

In the first coating stage, the first coating material was mixed with the solid dispersed phase at an elevated temperature T_{MAX-1} . After obtaining a homogeneous mix, the melt was cooled down to the temperature T_{C1} just above the melting point of the first coating material and a crumbling agent was added. Cooling was continued until the temperature of T_{MIN} was reached. In the second coating stage, the temperature of the particles from the first stage was raised to T_{MAX-2} and the second coating material was added at this temperature. Mixing was continued until the agglomeration of the particles was observed. At

15

this stage the temperature was lowered to a temperature T_{C2} just above the melting point of the second coating material and a small amount of crumbling agent was found to be sufficient to obtain crumbling. These double coated particles were then cooled to ambient temperature while continuing to mix.

20

In the Examples 4.2 and 4.4, the crumbling agents used in the first coating stage can create large amounts of heat and also act as water sink upon exposure to water.

25

30

35

40

45

50

55

TABLE 4

Example No.	First Coating Stage					Second Coating Stage				
	Material(s)	Solid Dispersed Phase	Crumbling Agent	T_{MAX} ($^{\circ}C$)	T_{C1} ($^{\circ}C$)	T_{MIN} ($^{\circ}C$)	Material(s)	Crumbling Agent	T_{MAX-2} ($^{\circ}C$)	T_{C2} ($^{\circ}C$)
4.1	10% PEG 12000 2% OPE (60 $^{\circ}C$)	52% Arosurf TA 100 (75 $^{\circ}C$)*	6% Aerosil 380	70	65	30	24% Paraffin Wax (49 $^{\circ}C$)	6% Aerosil 380	55	50
4.2	16% PCL (60 $^{\circ}C$)*	50% SDDCA	15% TSPP	75	65	30	16% PCL-diol (45 $^{\circ}C$)*	3% Aerosil 380	50	45
4.3	20% PCL (60 $^{\circ}C$)	48% SDDCA	10% Aerosil 380	75	65	30	20% PCL-diol (45 $^{\circ}C$)*	2% Aerosil 380	50	45
4.4	18% Paraffin Wax (71 $^{\circ}C$)	50% SDDCA	10% LiCl	80	72	30	18% Paraffin Wax (49 $^{\circ}C$)*	3% Aerosil 380	55	50

Key for Examples 4.1 to 4.4

Number inside brackets indicates melting point.

T_{MAX-1} , T_{MAX-2} = maximum temperature in the mixer during the 1st and 2nd coating stages.

T_{C1} , T_{C2} = temperature at which crumbling agent is added in the 1st and 2nd coating stages.

T_{MIN} = minimum temperature reached in the mixer after the 1st coating stage.

Examples 5.1 to 5.4

5

Particles were prepared having compositions in accordance with Table 5 below. These include both solid and liquid disperse phases. For these particles the polymeric material could contain a suitable surfactant while the silicone fluid or paraffin wax which constituted the liquid disperse phase could also contain surfactant. The general procedure was that the polymeric material was first heated with its surfactant (if any) to obtain a mixture of the two. The liquid phase was separately heated with its surfactant (if any) to obtain a mixture of the two. After incorporating the surfactants, if any were used, the polymeric material and liquid disperse phase were heated together and mixed to form an emulsion.

The emulsification was carried out in a static mixer which consists of a series of short capillaries separated by flow dividers to prevent channelling of the fluid. The capillary diameter (D), capillary length (L), capillary entry angle (θ_1), capillary exit angle (θ_2), total flow rate of the continuous and dispersed phases (Q) and the number of capillary units (N) are important factors in achieving small dispersed phase droplet particles ($<10\mu\text{m}$) with a narrow size distribution. Since the viscosity of the silicone antifoams and silicone fluid used in the Examples 5.1 to 5.5 is extremely large compared with the continuous phase viscosity, it is necessary to use elongational flow fields to achieve emulsification. The above static mixer provides such a flow field in which the maximum rate of shear S_m and elongation E_m at each stage is calculated from:

$$S_m = (32Q/\pi D^3)$$

$$E_m = (16Q/\pi D^3) \sin(\theta_i/2) \quad i = 1 \text{ (entry)} \quad i = 2 \text{ (exit)}$$

The above equation indicates that the entry/exit angles should be large (i.e. $\theta_1 = \theta_2 = 180^\circ$) and in order to reduce the pressure drop across the mixer, L/D should be small. The emulsifications were carried out under the following conditions:- Number of capillary units, $N=8$, $D=1\text{mm}$, $L/D = 2$ and $E_m 3 \times 10^5 \text{ s}^{-1}$.

Emulsion emerging from the last capillary unit is sprayed on to the solid dispersed phase which was heated in the Z-blade mixer to the temperature of the emulsion. Mixing was continued until a homogeneous mix had been achieved.

Thereafter, as for Examples 1.1 to 1.21, the melt was cooled to a temperature T_C just above the melting point of the coating material, 65% of the crumbling agent was added and then when agglomeration was observed the remainder of the crumbling agent was added while cooling the melt to some 30°C below the melting point of the coating material.

It was observed that the inclusion of ethylene acrylic acid copolymer (AC 5120) in the coating material of Example 5.5 was very useful. Firstly, this copolymer acted as a very efficient emulsifier in emulsifying the silicone antifoam. Secondly, it increases the viscosity of the continuous phase in the emulsion thus helping to reduce its tendency to form a double emulsion and also to reduce the size of the dispersed silicone antifoam. Finally, it increases the hardness of the continuous phase once it has solidified.

40

45

50

55

TABLE 5

Example No.	Coating Materials (Emulsion)				T _g (°C)	Solid Dispersed Phase	Crumbling Agent	T _c (°C)
	Continuous Phase		Liquid Dispersed Phase					
	Coating Material(s)	Surfactant	Liquid	Surfactant				
5.1	2% PEG 600 32% PEG 4000 6% PEO 200000	2% DC193	12% Silicone Antifoam	0.5% DC193	75	43% Light Soda Ash	2.5% Aerosil 380	65
5.2	1% PEG 600 20% PEG 4000 4% PEO 200000	0.5% DC193	7% Silicone Antifoam	0.5% DC193	75	58% TAED	9% Aerosil 380	65
5.3	18% PEG 12000	-	12% Paraffin Wax (49°C)*	1% Span 85	75	64% TAED	5% Aerosil 380	65
5.4	20% Paraffin Wax (60°C)*	1% DC193	10% Silicone Fluid 12500CS	1% DC193	70	60% Arosurf TA 100	8% Aerosil 380	65
5.5	10% AC 5120 15% Synper - onic A7	-	10% Silicone Antifoam	-	95	55% Light Soda Ash	10% Light Soda Ash	50

* Bracketed number indicates melting point

Particle Sizes

The average size and size distribution of the coated particles were found to depend on a large number of factors. These are: (1) raw material characteristics such as size, concentration and surface chemistry of the solid dispersed phase particles and crumbling agent, and molecular weight and chemistry of the coating material(s). (2) process conditions such as rotational speed of the mixer blades, temperature of the mixer when the crumbling agent is added and the type of mixer. In Table 6, the average size and size distribution of the particles illustrated by various Examples are tabulated.

TABLE 6 :

PARTICLE SIZE DISTRIBUTION AND AVERAGE PARTICLE SIZE										
Size Range (μm)	Particle Size Distribution of the Solid Dispersed Phase				Particle Size Distribution of the Product Particles Prepared According to Example No:					
	TAED	NaCl	SDDCA	Arosurf TA 100	1.6	2.1	1.19	3.1	4.1	4.3
> 2000	-	-	-	-	18.3	39.1	9.1	14.7	33.9	-
2000-1000	-	-	-	-	27.0	17.8	16.0	5.7	22.5	10.4
1000-710	0.9	0.1	-	-	16.2	8.9	6.5	18.1	11.3	8.1
710-500	1.3	5.1	-	9.4	10.9	14.5	15.5	8.7	10.3	24.8
500-355	9.1	47.6	0.5	40.9	7.9	11.5	15.7	21.4	8.5	23.6
355-250	7.8	29.1	2.5	31.0	6.6	5.0	12.3	5.5	10.0	18.1
250-180	36.7	12.8	3.0	12.1	4.7	2.0	14.6	24.9	1.8	9.6
180-125	30.5	3.1	1.8	4.6	4.6	0.7	7.5	0.5	1.6	3.9
125-45	13.0	1.8	6.3	2.0	3.8	0.5	2.8	0.5	-	1.5
< 45	0.7	0.4	85.9	-	-	-	-	-	-	-
Average size (μm)	247	387	7.1	393	1220	1598	771	1073	1481	638

Release Characteristics

The release characteristics of various encapsulated particles placed in water were determined by monitoring the concentration of the dispersed phase material in water as a function of time. Final concentration of the dispersed phase material after a prolonged time was also determined. The release profiles of the particles are expressed here as:- (1) delay time (t_0) (if any) before release commences; (2) initial rate of release (R_0 ; percent release per unit time) and (3) half life of the encapsulated dispersed phase ($t_{1/2}$). These values are tabulated in Table 7. As seen in this Table, considerable variations in delay time, initial release rate and half life of the dispersed phase can be obtained.

TABLE 7 :
RELEASE CHARACTERISTICS OF VARIOUS ENCAPSULATED MATERIALS

Capsules Prepared According to Example No:	Coating Materials		Dispersed Phase	Nominal Weight Percent of Dispersed Phase	Test Temp (°C)	Release Characteristics		
	First Coat	Second Coat				Delay Time t_0 (min)	Initial Release Rate R_0 (%/min)	Half Life $t_{1/2}$ (min)
TAED 1.3	-	-	TAED	100	25	0	3.3	17
	PEG 35000	-	TAED	60	25	0	3.1	18
1.6	PEO 200000	-	TAED	65	25	5	0.34	220
	PCL	-	TAED	64	25	0	0.98	60
5.4	AC 680	-	TAED	100	50	0	23.3	2
	PEG 12000 Wax (49°C)	-	TAED	65	50	0	6.25	33
TAED 1.6	-	-	SDDCA	60	25	0	66.7	1.2
	PCL	PCL-diol	SDDCA	48	25	0	7.5	30
1.19	PCL	Wax (49°C)	Arosurf TA 100	52	25	30	1.3	80
4.3	PEG 12000	-						
4.1	OPE (60°C)	-						

Notes on Table 7

5

1. Release of TAED in water is carried out at pH = 11.
2. Release of SDDCA in water is determined from the measurement of available chlorine.
3. Release of Arosurf TA 100 in water is determined from optical density measurements.

10 Example 6

Coated particles were prepared generally in accordance with Example 1.22 but using different coating materials. In some instances the coated particles were coated again with a second coating material. In contrast to Example 4, both coating materials were water-soluble. The release of antifoam from the resulting particles was determined by monitoring change in surface tension at 25 °C and/or by monitoring the foam controlling action of the particles.

Results are set out in Table 8 below.

Particles in accordance with Examples 6.2 and 6.3 were also subjected to agitation in a powder mixer for 15 minutes to test the durability of the coating. The release of antifoam was not altered for Example 6.3 particles, and increased only slightly for particles of Example 6.2, thus illustrating the durability of their coatings.

25

30

35

40

45

50

55

TABLE 8

Example No	Coating Material First Coat	Coating Material Second Coat	Release Characteristics	Foam Controlling Action at 40°C
Control	-	-		
6.1	25% PEG 6000 ML	-	Fast release at 25°C (half life 4 minutes).	Complete suppression of foaming at 40°C.
6.2	14% sodium stearate 14% lauric acid	-	Almost no release at 25°C. Fast release at 40°C	Complete suppression at 40°C.
6.3	10% sodium stearate 10% lauric acid 8% AC 5120	-	No measurable release at 25°C. Fast release at 40°C.	Almost complete suppression at 40°C.
6.4	22% PEG 6000 DS	15% PEG 200	}	Complete suppression of foaming at 40°C.
6.5	7.5% sodium stearate 7.5% lauric acid	10% PEG 1000		
6.6	5.5% sodium stearate 5.5% lauric acid 1% AC 5120	11% PEG 1000		

Claims

1. A process for coating or encapsulating solid particles and/or liquid droplets, the process comprising a first step of forming a melt of a coating material with the said particles and/or droplets as a disperse phase therein, and a second step of destabilizing the melt by addition of solid particles and/or by cooling, causing the melt to crumble to a particulate product whereof the particles comprise the coating material with the particles and/or droplets of the disperse phase embedded therein.

2. A process according to claim 1 wherein the coating material is an organic polymeric material, wax, soap, non-soap surfactant, fatty acid or a mixture of such materials.

3. A process according to claim 2 wherein the coating material is water-soluble or water-swellaible.

4. A process according to claim 2 wherein the coating material is water-insoluble.

5. A process according to any one of claims 1 to 4 wherein solid particles encapsulated by the process

are themselves water-soluble.

6. A process according to any one of claims 1 to 5 wherein solid particles encapsulated by the process are a bleaching compound.

7. A process according to any one of claims 1 to 5 wherein solid particles encapsulated by the process
5 are a bleach activator.

8. A process according to any one of claims 1 to 5 wherein liquid droplets encapsulated by the process are antifoam agent and/or fabric softener.

9. A process according to any one of the preceding claims wherein both liquid droplets and solid particles are encapsulated together.

10. A process according to any one of claims 1 to 5 wherein solid particles encapsulated by the process
10 are porous and have a liquid absorbed therein.

11. A process according to claim 10 wherein the liquid is a perfume.

12. A process according to claim 10 wherein the liquid is an antifoam.

13. A process according to any one of the preceding claims wherein the particulate product particles
15 are further coated with an outer coating.

14. A process according to claim 13 wherein the further coating is carried out by repeating the steps of claim 1 with the said product particles as the disperse phase.

15. A process according to claim 13 or claim 14 wherein the particles which receive an outer coating are water-swellable.

20

25

30

35

40

45

50

55

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 382 464 A3

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **90301208.6**(51) Int. Cl.⁵: **C11D 17/00, C11D 3/37**(22) Date of filing: **06.02.90**(30) Priority: **09.02.89 GB 8902909**(43) Date of publication of application:
16.08.90 Bulletin 90/33(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE(68) Date of deferred publication of the search report:
28.10.92 Bulletin 92/44(71) Applicant: **UNILEVER PLC**
Unilever House Blackfriars
London EC4P 4BQ(GB)(84) **GB**(71) Applicant: **UNILEVER N.V.**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)(84) **CH DE ES FR IT LI NL SE**(72) Inventor: **Akay, Galip**
36 Gulls Way
Heswall, Wirral L60 9JQ(GB)(74) Representative: **Ford, Michael Frederick et al**
MEWBURN ELLIS 2 Cursitor Street
London EC4P 4BQ(GB)(54) **Coating Process.**

(57) A coating process can serve to encapsulate either solid particles or liquid droplets or both. The process comprises a first step of forming a melt of a coating material in which the solid particles or liquid droplets as a dispersed phase. This melt is then destabilised by adding solid particles and/or by cooling. This causes the melt to crumble to a particulate product consisting of dispersed phase encapsulated with the coating material.

Examples of coating material are organic polymers, soap fatty acid mixtures and non-soap surfactants. Materials which can be encapsulated include bleaching agents and perfume.

EP 0 382 464 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 1208

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,P X,L	EP-A-0 303 416 (UNILEVER NV) * Whole document * Document so quoted for it's casting doubt on the "first-deposit" characters of GB-A-8 902 909 and thus validity of the convention-priority claim	1-4	C 11 D 17/00 C 11 D 3/37
Y	---	5-7,13-15	
X	FR-A-2 029 842 (N. SALKIN) * Whole document *	1-3	
Y	---	5-7,13-15	
Y	EP-A-0 051 987 (THE PROCTER & GAMBLE CO.) * Whole document *	5-7,13-15	
A	---	2,3,8	
X	FR-A-2 123 476 (LAPORTE INDUSTRIES LTD) * Page 1, line 1 - page 2, line 13, page 2, line 23 - page 3, line 33; page 4, line 20 - page 6, line 10, page 7, lines 5-10; page 8, lines 2-5; page 9, lines 25-30; table, examples 14,16; claims 1,3-11 *	1-7,13	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
Y	---	14,15	C 11 D
Y	DE-A-2 431 581 (HENKEL & CIE GmbH) * Whole document *	5-7,13-15	
A	---	1-4	
	---	-/-	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12-06-1992	Examiner FISCHER W.H.F.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	



European Patent
Office

EUROPEAN SEARCH REPORT

Page 2

Application Number

EP 90 30 1208

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	FR-A-2 281 160 (NOBEL HOECHST CHIMIE) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12-06-1992	Examiner FISCHER W.H.F.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			